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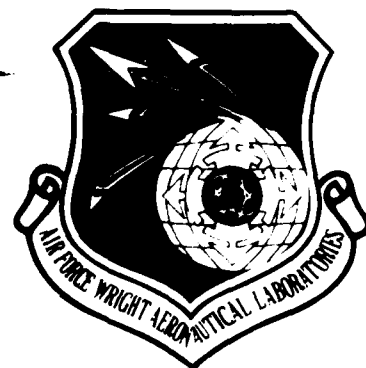
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MEASUREMENT OF ELECTRON EXCITATION OF THE $a^1\Delta_g$ STATE OF O_2
USING THE SWARM TECHNIQUE

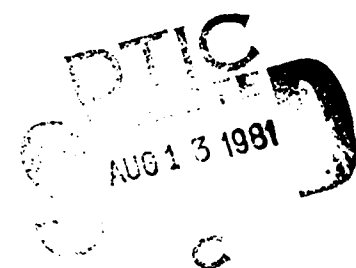


K. TACHIBANA AND A. V. PHELPS

QUANTUM PHYSICS DIVISION
U.S. BUREAU OF STANDARDS
BOULDER, CO 80303

MAY 1981

FINAL REPORT FOR PERIOD OCTOBER 1979 - SEPTEMBER 1980



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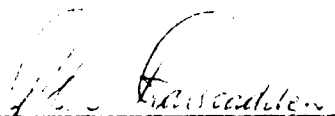
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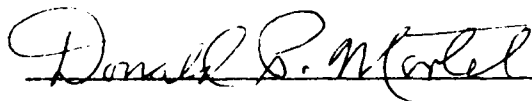
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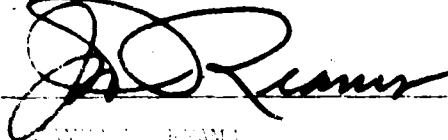


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Measurements have been made of electron excitation coefficients for the $a_1\Delta_g$ metastable state of O_2 . The measurements were made in mixtures 1 and 5% O_2 in Ar for mean electron energies between about 0.9 and 4 eV. The measured excitation coefficients are about 30% above predictions for 1% O_2 and about 30% below predictions for 5% O_2 . The measured rate coefficient for quenching of the $O_2(a_1\Delta_g)$ state by O_2 is in good agreement with the literature value, but the rate coefficient for quenching by Ar is about twice previously published values.		

PREFACE

This work was performed in the Quantum Physics Division, U.S. Bureau of Standards, at the Joint Institute for Laboratory Astrophysics under MIPR FY1455-80-00607. Dr. Tachibana was at the Joint Institute for Laboratory Astrophysics while on leave from the Department of Electronics, Kyoto Technical University, Kyoto, Japan. This work was performed during the period October 1979 through September 1980 under Project 2301 Task S2, "Plasma Research, Gas Discharge and Laser Plasmas." The Air Force contract manager was Dr. Alan Garscadden, Energy Conversion Branch, Aero Propulsion Laboratory.

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SECTION I

INTRODUCTION

The metastable states of O_2 such as $a^1\Delta_g$ and $b^1\Sigma_g^+$ have important roles not only in the earth's atmosphere but also in lasers of the excitation-energy transfer type, e.g., the O_2 -iodine molecular laser. A previous paper¹ (hereafter referred as I) reported a measurement of the coefficients for electron excitation of the $b^1\Sigma_g^+$ state as a function of the ratio of the electric field to the gas density E/N using a drift tube technique. At that time it was not possible to measure the excitation coefficients for the $a^1\Delta_g$ state mainly because of the extremely small radiative transition probability of the state and the lack of a high sensitivity and low noise detector for the 1.27 μm radiation emitted in the (0-0) band of the $a^1\Delta_g - X^3\Sigma_g^-$ transition. In the meantime, we have been able to purchase a suitable IR detector and have used it to measure the rate coefficients for the $O_2(a^1\Delta)$ state.

The experimental measurement and subsequent analysis of electron excitation coefficients for the $O_2(a^1\Delta_g)$ state is an important step in the development of one's ability to use collision cross section data to predict and optimize the operation of electrical discharges in gas mixtures containing oxygen. There is fair agreement among the determinations of the cross section for direct excitation of the $O_2(a^1\Delta_g)$ state by electron beam techniques.² Therefore, the objectives of these measurements are to test these cross sections for swarm or discharge conditions, to measure the contribution of cascading to the $O_2(a^1\Delta_g)$ state excitation, and to determine experimentally the relative importance of competing excitation processes such as vibrational excitation. Throughout the analyses of this data, we must look for clues as to the source of the large discrepancy between measured and predicted excitation coefficients

for the $O_2(b^1\Sigma_g^-)$ state which were found by Lawton and Phelps¹ and attributed to an unexpected cascading from the higher metastable states, e.g., the $c^1\Sigma_u^-$ state.

Most of the theory of the experiment and procedure given in I can be used in this experiment. We, therefore, summarize very briefly in Section II the equations relating the observed signal to the excitation coefficient. Somewhat more detailed descriptions are given in Section II for the differences in the experiments caused by differences in the detectors. The rate coefficients for quenching of the $a^1\Delta_g$ state by O_2 and by Ar are given in Section III. In Section IV the excitation rate coefficients for the state are given as a function of E/N and are compared with the theoretical predictions.

SECTION II

EXPERIMENTAL TECHNIQUE

A schematic of the drift tube technique used for determination of excitation coefficients for the $O_2(a^1\Delta_g)$ state is shown in Fig. 1. A continuously operating 100 W high pressure mercury lamp is passed through broad band interference filters centered at 190 nm (not shown) and then through a quartz window coated on the inside with a semi-transparent cathode film of evaporated Pd-Au. The resulting photoelectrons enter the gas filled, parallel plate drift tube. The anode voltage is modulated so as to periodically apply a known electric field E and so produce electrons with a modulated mean energy. These electrons may excite the O_2 molecules to the $a^1\Delta_g$ state. Since the radiative lifetime of these metastables is very long (3900 sec), most of the metastables will be destroyed by diffusion to the drift tube electrodes or by collisional quenching by the O_2 molecules or by the Ar atoms used to reduce the diffusion loss. At best, about one molecule in 2000 is able to radiate at 1.27 μ m.

A very brief outline of the theory relating the radiated power P at 1.27 μ m reaching the detector from the drift tube is given next. Thus, the power is given by

$$P = h\nu A \frac{\Delta\Omega}{4\pi} \int_V \eta[a]dV, \quad (1)$$

where $h\nu$ is the photon energy, A is the measured radiative transition probability³ as corrected for collision induced radiation by the Ar buffer gas,⁴ $\Delta\Omega$ is the solid angle of the detector as seen from the center of the drift tube and η is the efficiency of photon collection from various parts of the drift tube relative to that at the center. The density of $O_2(a^1\Delta_g)$ metastables $[a]$ is obtained from the solution of the continuity equation

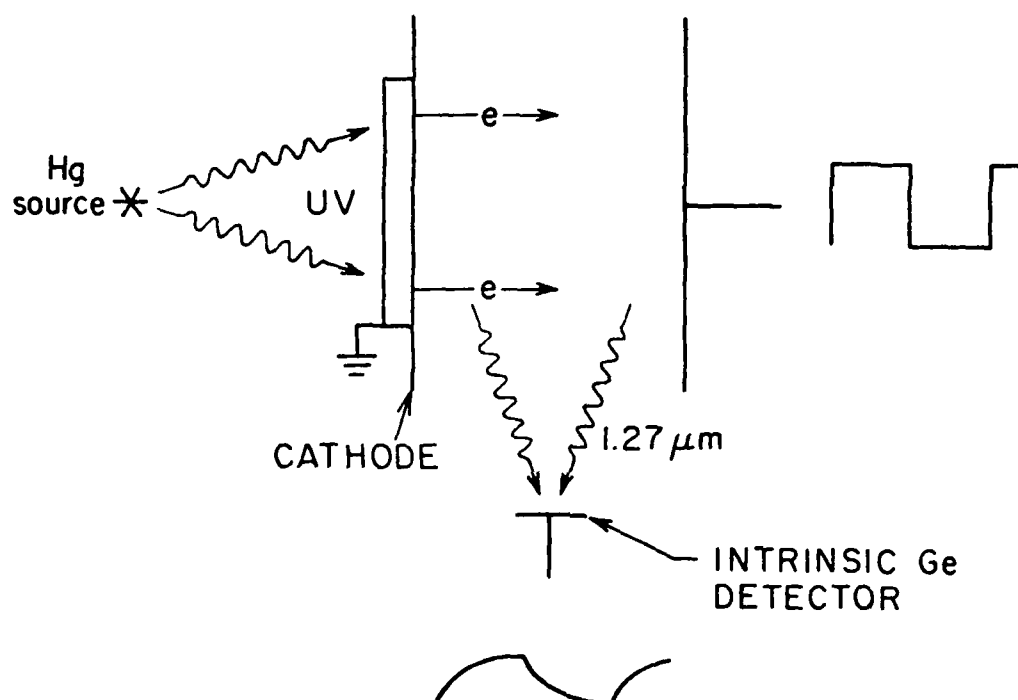


Figure 1. Schematic of Experiment.

$$\frac{d[a]}{dt} = DV^2[a] - (k_d N + A)[a] + k_e N n_e, \quad (2)$$

where D is the effective metastable diffusion coefficient, k_d is the effective rate coefficient for metastable destruction by O_2 and by Ar at the total gas density N , and n_e is the electron density n_e . Here the electron excitation rate coefficient k_e is given by

$$k_e = \int_0^\infty v Q_a(\epsilon) \epsilon^{-2} f(\epsilon) d\epsilon, \quad (3)$$

where v and ϵ are the electron speed and energy, $Q_a(\epsilon)$ is the cross section for electron excitation of the $O_2(a^1\Delta_g)$ state, and $f(\epsilon)$ is the normalized electron energy distribution. Here we assume that any excitation of the $O_2(a^1\Delta_g)$ state by cascading from higher excited states is rapid on the time scale of these experiments and is included in k_e .

The coefficients describing the destruction of metastables in this experiment are determined from measurements of the time dependence of the 1.27 μm emission. The diffusion term in Eq. (2) adds greatly to the difficulty of quantitative analysis of the emission data and the reader is referred to 1 for a detailed discussion. For the present purposes we will limit the discussion to high gas densities where

$$\gamma = k_d N \gg A + D(\pi/L)^2, \quad (4)$$

where L is the distance between the drift tube electrodes. In this limit the metastable density is given by

$$[a] = \frac{k_e N n_e}{\gamma} (1 - e^{-\gamma t}) = \frac{e j_e}{e \gamma} (1 - e^{-\gamma t}), \quad (5)$$

where $k_e N = e w_e$ and e , w_e and j_e are the electron charge, drift velocity and current density. The radiated power reaching the detector from the drift tube reaches its maximum value P_{max} when $\gamma t \gg 1$ and is given by

$$P_{\max} = \frac{h\nu A}{e} \frac{\alpha L}{\gamma} \frac{G}{q} i, \quad (6)$$

where i is the total current through the drift tube and G and q are geometrical and current correction factors defined in I.

The drift tube shown in the detailed schematic of Fig. 2 is the same as the one used in I. The electrode spacing was 38.4 mm and the cathode area was 0.28 m^2 . The period of the zero-based square wave anode voltage was varied from 10 to 25 sec depending on the decay constant of the $a^1\Delta_g$ state. This data recording period was followed by a dead time of 15 sec for the computer processing as described below. The accelerating voltage ranged from 111 to 1152 V and the total current in the on-period was 0.02 to 0.09 μA .

Measurements were made with 0.1 to 5% O_2 in Ar at the total gas densities of 10^{24} to $2 \times 10^{25} \text{ m}^{-3}$. The reason for using dilute O_2 in Ar at relatively high pressure is that we expected to increase the detection efficiency of $1.27 \mu\text{m}$ radiation by decreasing the non-radiative losses of $a^1\Delta_g$ states due to the diffusion, i.e., by using Ar it is possible to reduce the O_2 density and resultant quenching by a factor of ten. After O_2 of 99.99% specified purity was bled into the drift tube from a liquid- N_2 cooled reservoir, Ar of 99.999% purity was bled into the tube directly from a high pressure cylinder.

A liquid- N_2 cooled intrinsic germanium detector (North Coast Model 403L) was mounted at the top of the drift tube. The specified responsivity and NEP (noise equivalent power) of the detector are $7 \times 10^9 \text{ V/W}$ and $1 \times 10^{-15} \text{ WHz}^{-1/2}$ at $1.3 \mu\text{m}$. The typical "DC response" for a squarewave IR input signal, the width of which is comparable to the real signal, is shown in Fig. 3.

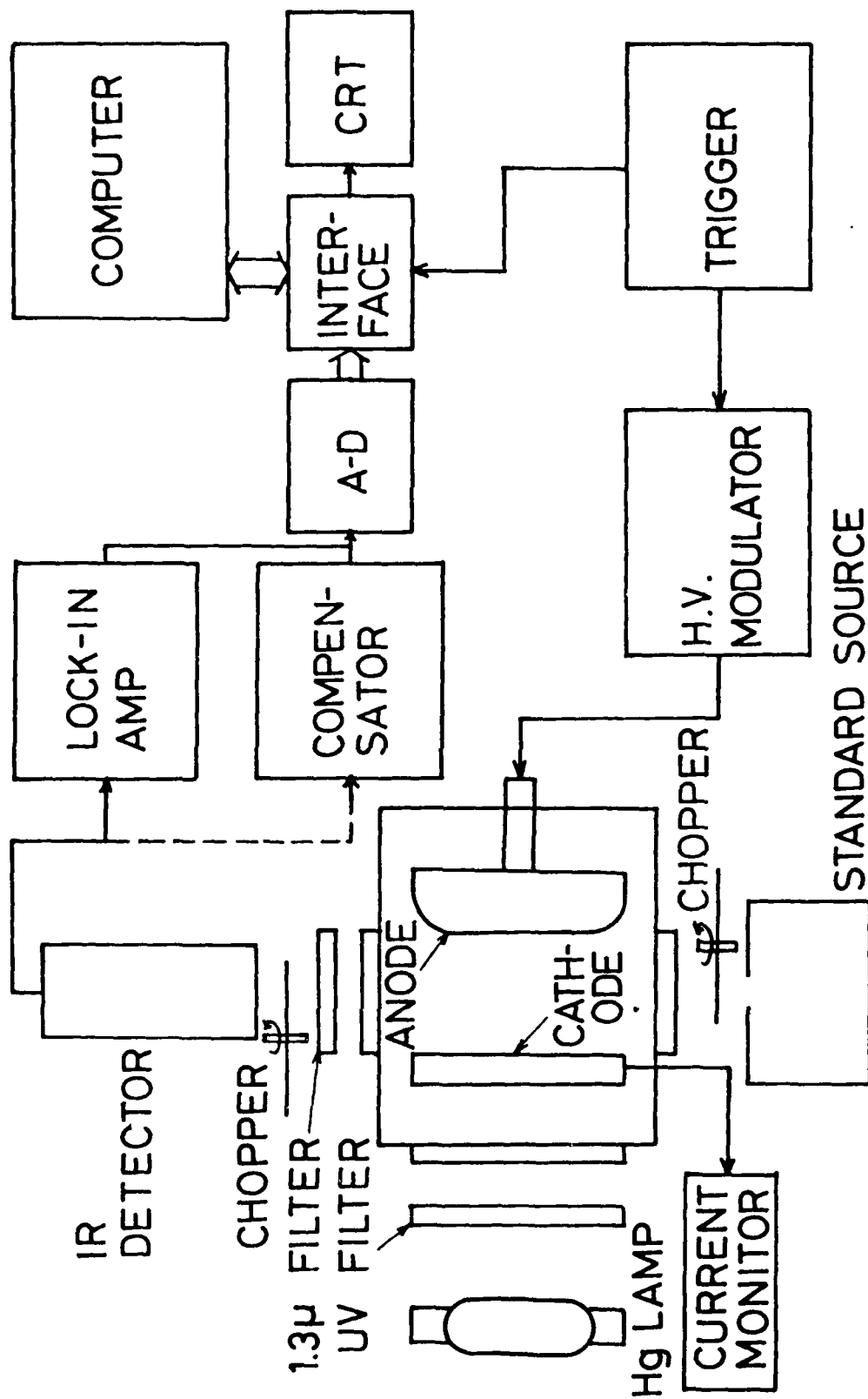


Figure 2. Detailed Schematic of Apparatus.

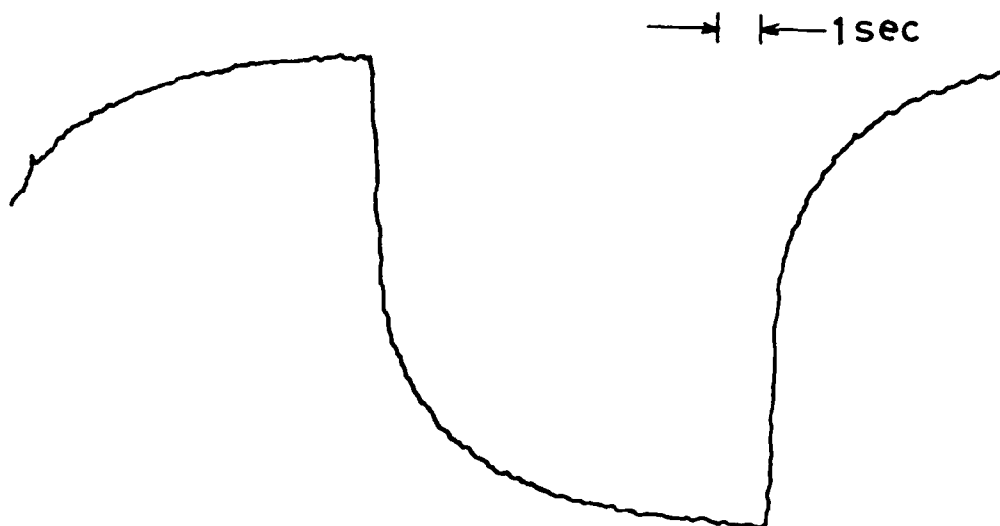


Figure 3. Detector Response to Square Wave IR Signal.

The response consists of fast and slow components, the time constants of which were about 10 msec and 3 sec, respectively. Two techniques have been used to overcome this problem. One way is to use only the fast response part by chopping the signal in front of the detector at a frequency of about 100 Hz and detecting the output signal through a lock-in amplifier. This method is referred to as AC-method hereafter and is shown schematically in Fig. 4. The other way is to use an amplifier which compensates for the 3 sec response and partially compensates for the 10 msec response. This was possible with a circuit as shown in Fig. 5.

Figure 5 also shows the current waveforms at the points indicated. This is a kind of feed-forward compensation and referred to as compensated DC-method hereafter. A merit of the DC-method is that we were able to get a higher S/N ratio and responsivity than with the AC-method, i.e., a factor of more than 2. A demerit is a rather critical adjustment of the compensation. However, we were able to check the compensation in the compensated DC-method using the AC-method at higher signal levels.

We encountered another problem due to spikes caused by cosmic rays, the heights of which were 5 to 20 mV at the output of the detector preamplifier. A representative AC-method signal from the detector is shown in Fig. 6. The width of a spike was usually only one sampling interval of the data recording system used, so that we were able to reject the spikes by a computer algorithm which replaced a sudden change in signal i.e., a spike, with the average value of the signal in adjacent channels.

A mini-computer was used as a data acquisition and analyzing system. The signal for the compensated amplifier or the lock-in amplifier was sampled every 40 to 200 msec depending upon the period of the anode voltage.

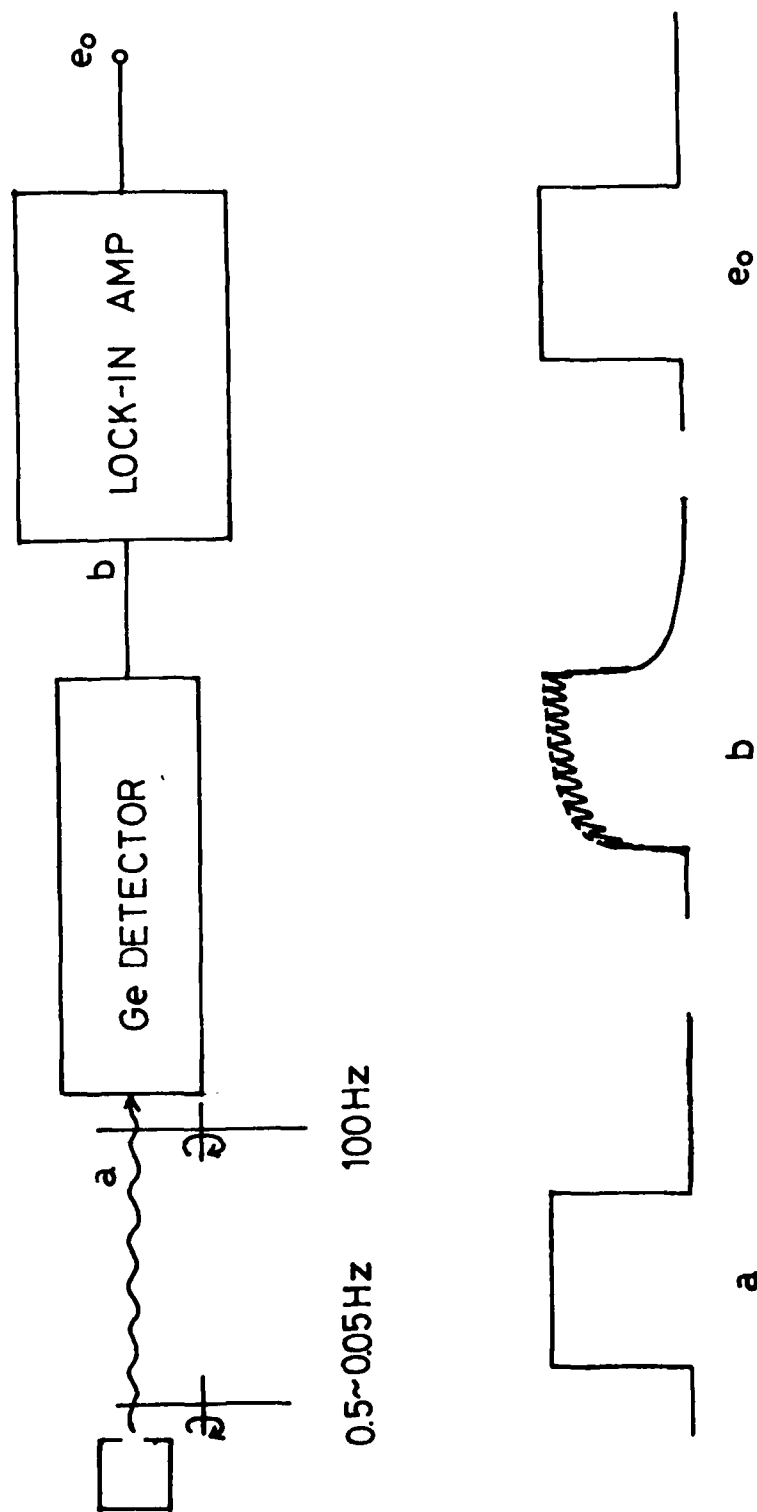


Figure 4. AC Mode of Detector Operation.

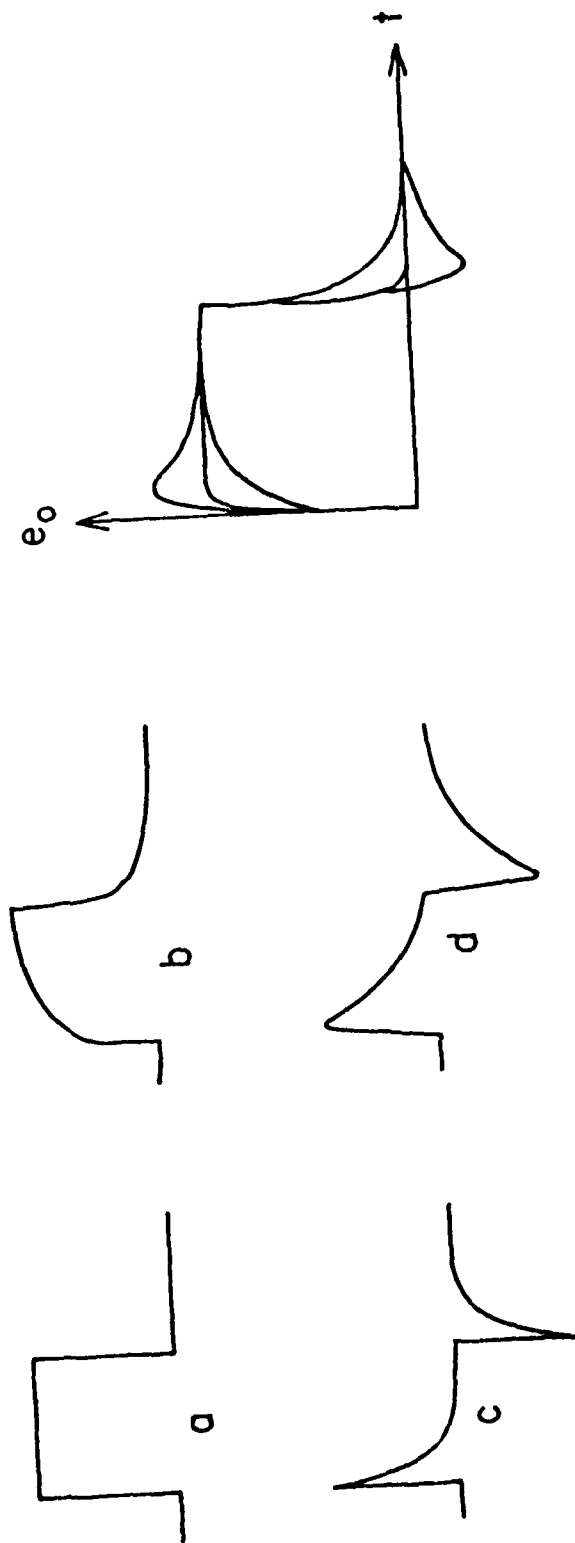
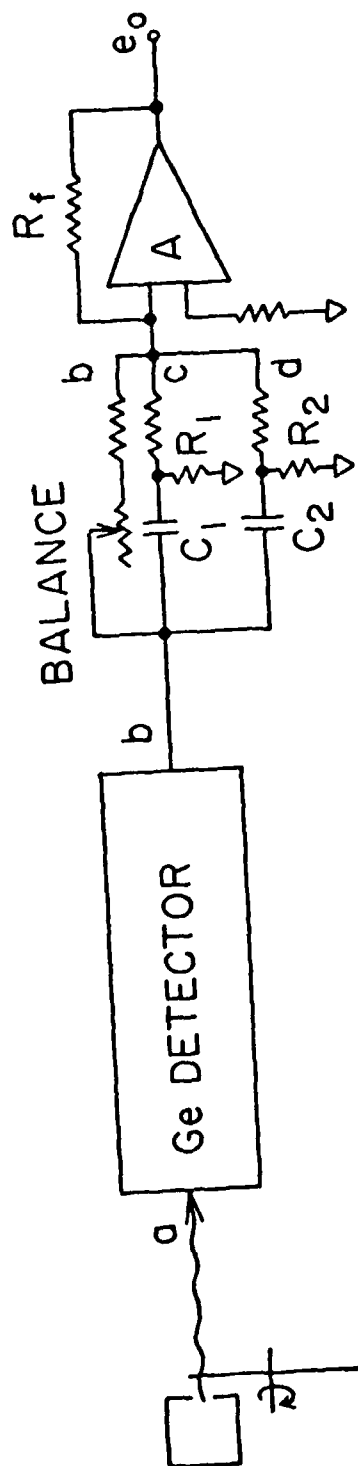


Figure 5. Compensated or "DC" Mode of Detector Operation.

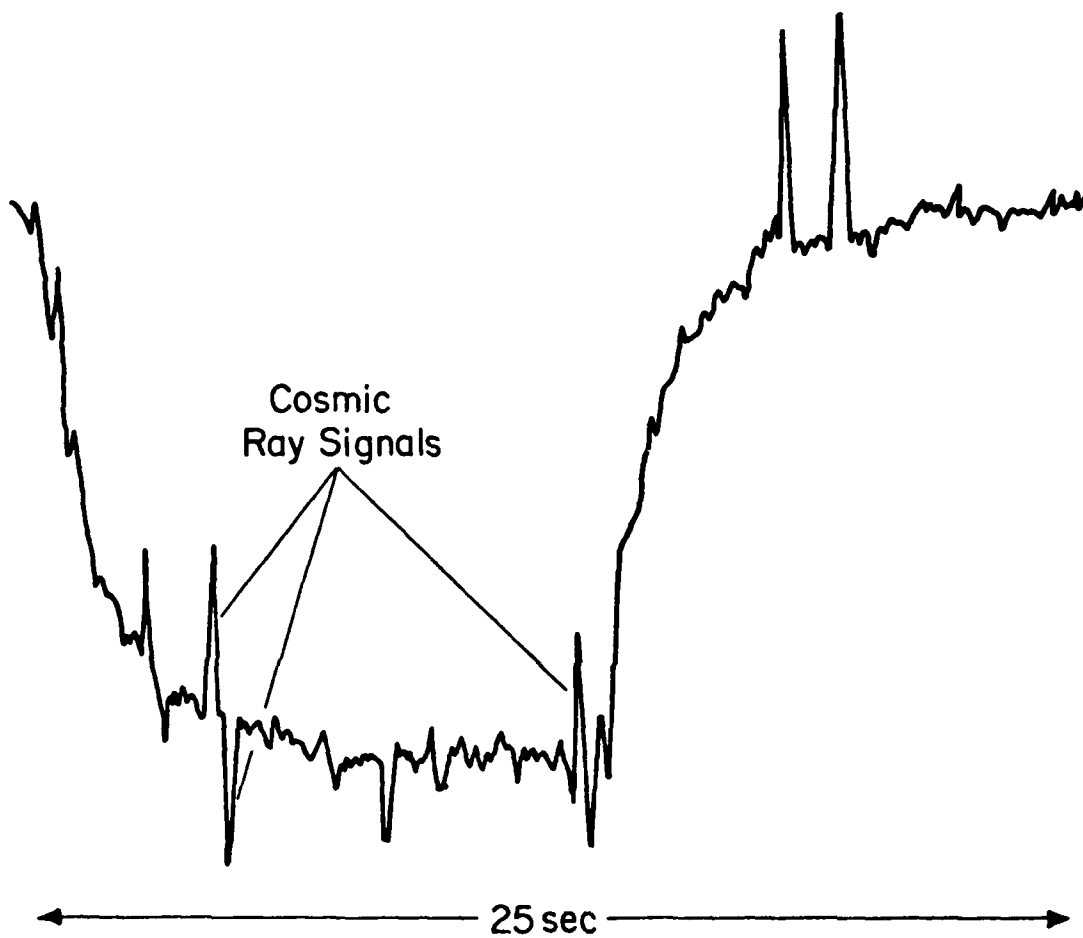


Figure 6. Representative Detector Output.

A set of data (256 points during a sweep) was stored in the computer and then analyzed to reject spikes due to cosmic rays. Sets of data were additively accumulated in the computer memory. After a desired number of sweeps (8-22) were completed, data was stored on a magnetic tape. The computer was also used to analyze the data by a least squares fitting procedure, and the data points as well as the fitted results were displayed on a CRT.

The (0-0) band of the $a^1\Delta_g \sim X^3\Sigma_g^+$ system at $1.27 \mu\text{m}$ was isolated from the background radiation by an interference filter with 75% peak transmission at $1.32 \mu\text{m}$ and a $0.147 \mu\text{m}$ FWHM. The value $\langle f_1 \rangle$ defined by Eq. (6) in I was calculated using the emission band profile of Wood et al.⁵ Although the necessary data on vibrational relaxation of the $v=1$ level of $O_2(a^1\Delta)$ to the $v=0$ level is not available,⁵ the near coincidence of wavelengths and transition probabilities for the 0-0 and 1-1 transitions⁷ means that our measurements are independent of the ratio of populations in the $v=1$ and $v=0$ levels of the $O_2(a^1\Delta)$ state.

The calibration of the detection system was done with a black-body light source mounted on the opposite side of the drift tube from the detector. An aperture of 1.50 mm diameter was placed in front of the source 0.47 m from the detector so as to reduce the black-body signal. When the temperature of the source was 213°C the intensity at the detector was comparable to that observed for the $O_2(a^1\Delta_g)$ emission. A chopper in front of the source modulated the black-body emission at a period of 20 sec, which was also comparable to that used for the $a^1\Delta_g$ emission.

The spatial variation of the detection efficiency was measured by a method similar to that described in I. A hollow sphere with a small aperture

covered by a diffuser was scanned over the drift region. The sphere was illuminated by a iodine-tungsten lamp through a quartz light pipe. The results show that the radially averaged detection efficiency $\eta(z)$ is given by

$$\eta(z) = 0.973 + 0.05 \sin(2\pi z/L) - 0.23(1-2z/L) . \quad (7)$$

The geometrical factor G is therefore given by

$$G = 0.973 G_A + 0.05 G_B - 0.23 G_C , \quad (8)$$

where G_A and G_C are the same as given in I. G_B is given by

$$G_B = \frac{2\pi a}{[a^2 + (2\pi)^2]} \frac{(d^2 + \pi^2)}{[d^2 + (2\pi)^2]} , \quad (9)$$

instead of Eq. (A1) in I. Here $d^2 = k_d NL^2/D$.

SECTION III

QUENCHING RATE COEFFICIENTS

Figure 7 shows a typical 1.27 μm signal as a function of time. The solid curves show the least squares fits to the data of functions of the form $a_1 + a_2 \exp(-a_3 t)$. The average value γ of the exponents obtained from rise and fall parts was assumed equal to the decay constant for the fundamental diffusion mode as in I. The decay constant γ is plotted versus the total gas density N for various O_2 -Ar mixtures in Fig. 8. The data points measured by the compensated DC-method, shown by circles are consistent with the points measured by the AC-method, shown by triangles. The radiative transition probability A for the 1.27 μm band is much smaller than γ , so that

$$\gamma = \pi^2 D / L^2 + k_d N_T. \quad (10)$$

Here the effective quenching rate coefficient k_d is given by $k_d^0 = (k_d^0 [\text{O}_2] + k_d^A [\text{Ar}])/([\text{O}_2] + [\text{Ar}])$, where k_d^0 and k_d^A are the quenching rate coefficients by O_2 and by Ar, respectively. In order to obtain D and k_d , we use a plot of γN vs N^2 . In this plot D is obtained from the intercept and k_d from the slope. This plot is shown in Fig. 9 for O_2 fractional concentrations of 1 and 5%. Circles and triangles are the same as for Fig. 8 and bars show the peak to peak errors. Both lines give the same intercept, from which the diffusion coefficient is determined to be $DN_T = (2.8 \pm 0.2) \times 10^{20} \text{ m}^{-1} \text{ sec}^{-1}$. This value is smaller than the value $4.9 \times 10^{20} \text{ m}^{-1} \text{ sec}^{-1}$ for pure O_2 measured by Vidaud, et al.⁸ We can determine k_d^0 and k_d^A from the two k_d values at different O_2 contents to be $k_d^0 = (1.67 \pm 0.1) \times 10^{-24} \text{ m}^3 \text{ sec}^{-1}$ and $k_d^A = (1.8 \pm 0.1) \times 10^{-25} \text{ m}^3 \text{ sec}^{-1}$. As seen in Table I, the value for k_d^0 agrees well with some of the recent measurements. However, the value for k_d^A is larger than recent measurements by about a factor of two. Because of the very small value of k_d^A and the high Ar densities used we are concerned that impurities may cause a significant error in our result.

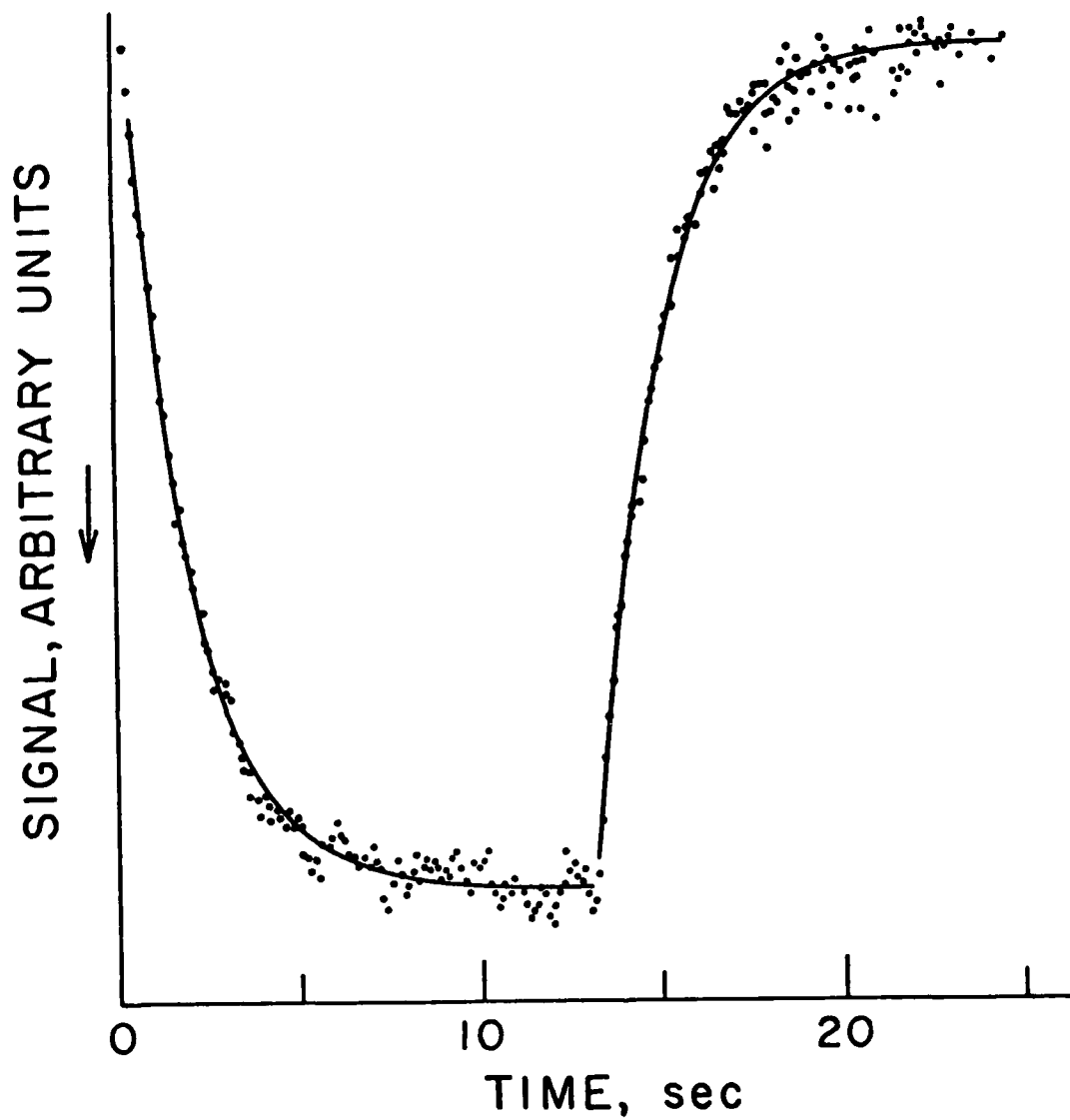


Figure 7. Example of Processed Data and of Fits of Exponential Rise and Fall.

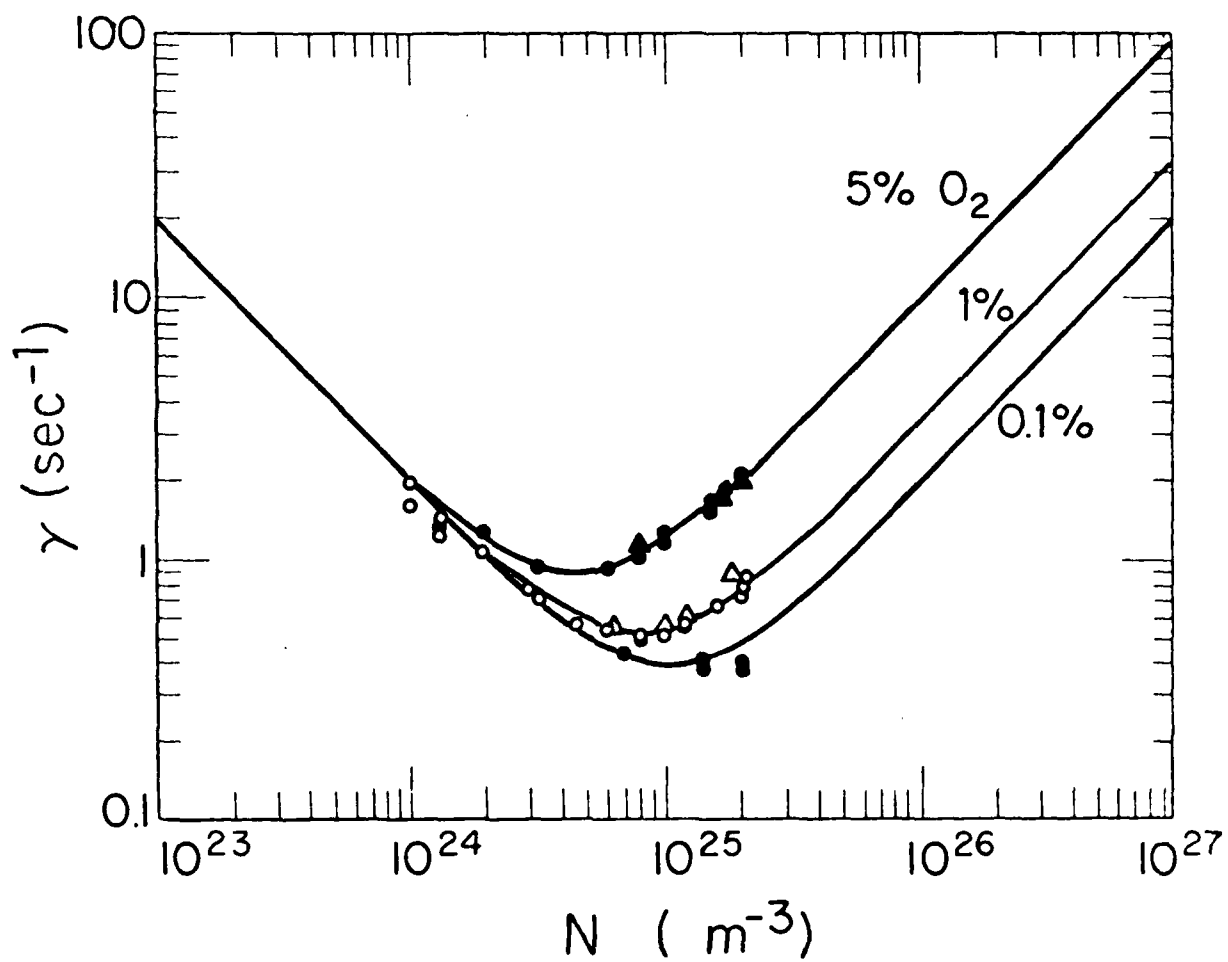


Figure 8. $\text{O}_3(\text{a}^1\Delta)$ Decay Constant vs Total Gas Density.

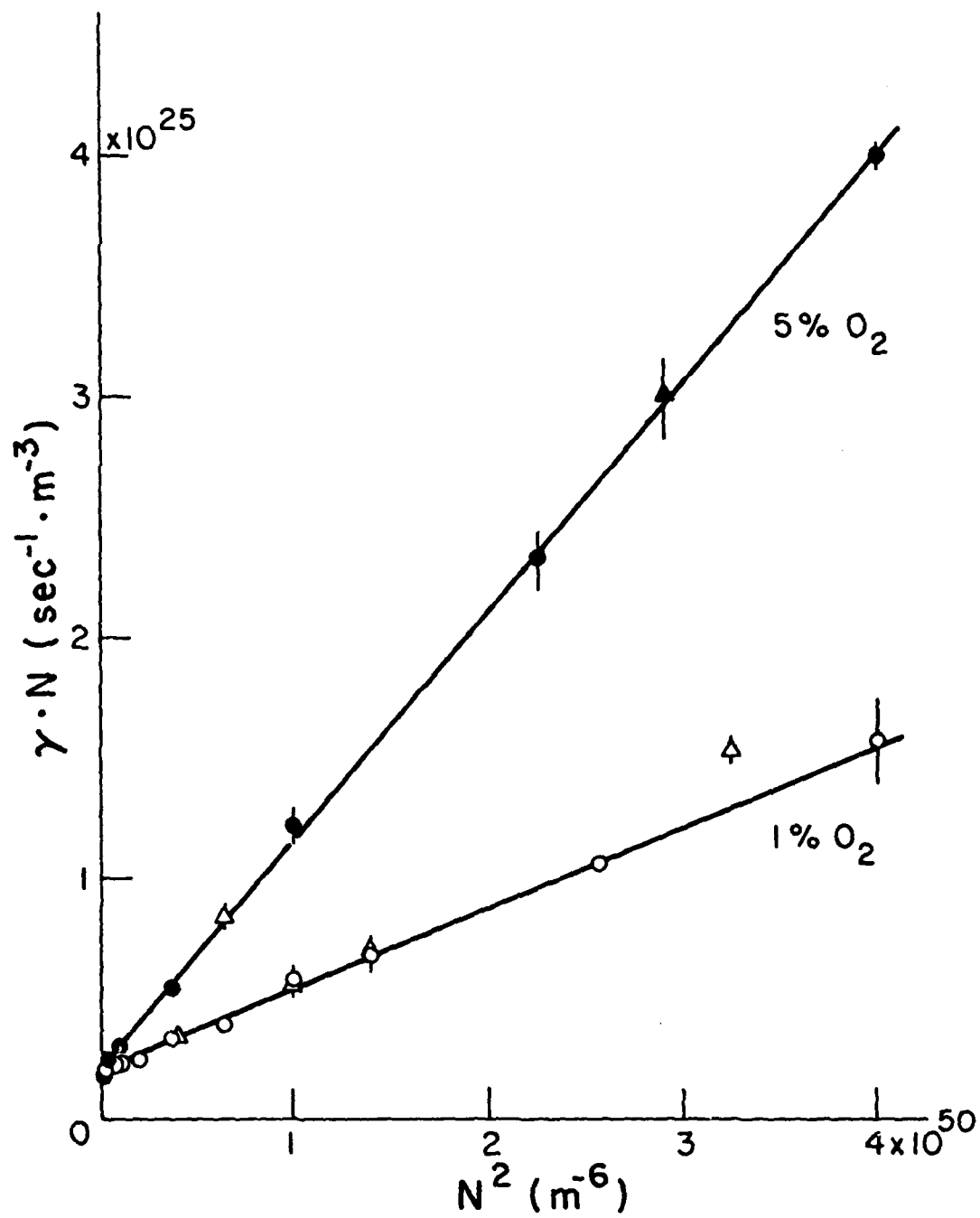


Figure 9. Determination of Quenching and Diffusion Coefficients.

TABLE 1
RATE CONSTANTS FOR QUENCHING OF $O_2(a^1\Delta_g)$ BY VARIOUS GASES*

quencher	this work	Ref. 9	Ref. 10	Ref. 11	Ref. 12	Ref. 13	Ref. 14	Ref. 15
O_2	1.57	1.47	1.56		1.7	2.22	2.4	2.04
N_2				0.14	≤ 0.01	< 0.003	≤ 0.11	0.042
H_2		4.15		5.3	3.7	4.53		
CO_2		≤ 0.013			0.08	0.015	3.9	
He				0.008	0.01	< 0.008		
Ar	0.018			0.009	0.01	< 0.008	≤ 0.21	
Kr				0.0079				
Xe				0.034				

* in units of $10^{-18} \text{ cm}^3/\text{sec.}$

SECTION IV

EXCITATION COEFFICIENTS

Figure 10 shows the excitation coefficients α/N as a function of N for a mixture of 1% O_2 and 99% Ar for two values of E/N . The solid circles were calculated using a refined form of Eq. (10), actually Eq. (17) in I, with $q=1$, $G=1$ and $A = 2.58 \times 10^{-4} \text{ sec}^{-1}$. The solid triangles show the data corrected by the appropriately calculated values of G and by the factor due to the effect of collision-induced transitions, that is, $\bar{A}/A = 1 + 0.258 \rho_A + 3.58 \rho_O$. Here \bar{A} is the effective radiative transition probability and ρ_A and ρ_O are the densities of O_2 and Ar in units of $2.69 \times 10^{25} \text{ atom/m}^3$. The factor for ρ_O is taken from Ref. 3 and that for ρ_A from Ref. 4, respectively. The open circles show the final results corrected by the q values calculated from Eq. (14) in I. The q -correction amounted to a factor of from 1 to 7, depending on the E/N and N values. For our conditions the departure of q from unity was caused by electron attachment, i.e., ionization was negligible. The corrected results for the rate coefficients at a fixed E/N value are independent of N except for some points at the lower E/N and lower N . This indicates that the attachment coefficients used in the calculation of q -values were reasonable. The final results for α/N are shown as a function of E/N in Figs. 11 and 12 for fractional O_2 concentrations of 1 and 5%, respectively.

The main differences in the sources of experimental error in the present measurements and those of I are as follows: the radiative transition probability for the $a^1\Delta_g$ state ($\sim 20\%$), least squares fitting of the waveform (10%), calibration using the black-body light source (10%) and the differences in the spectral sensitivity at $1.27 \mu\text{m}$ and at $1.35 \mu\text{m}$ where the convolution of

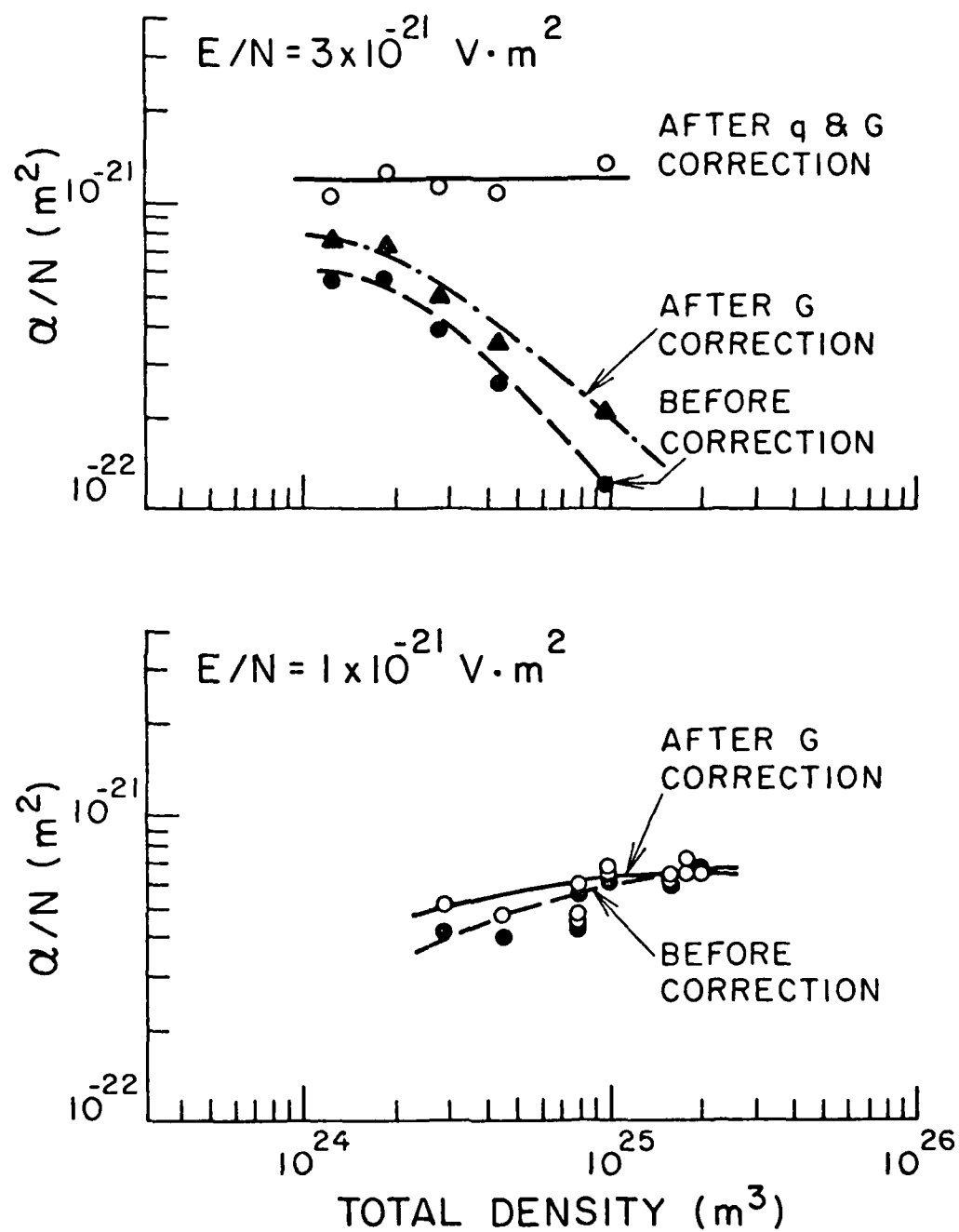


Figure 10. Gas Density Dependence of α/N Values.

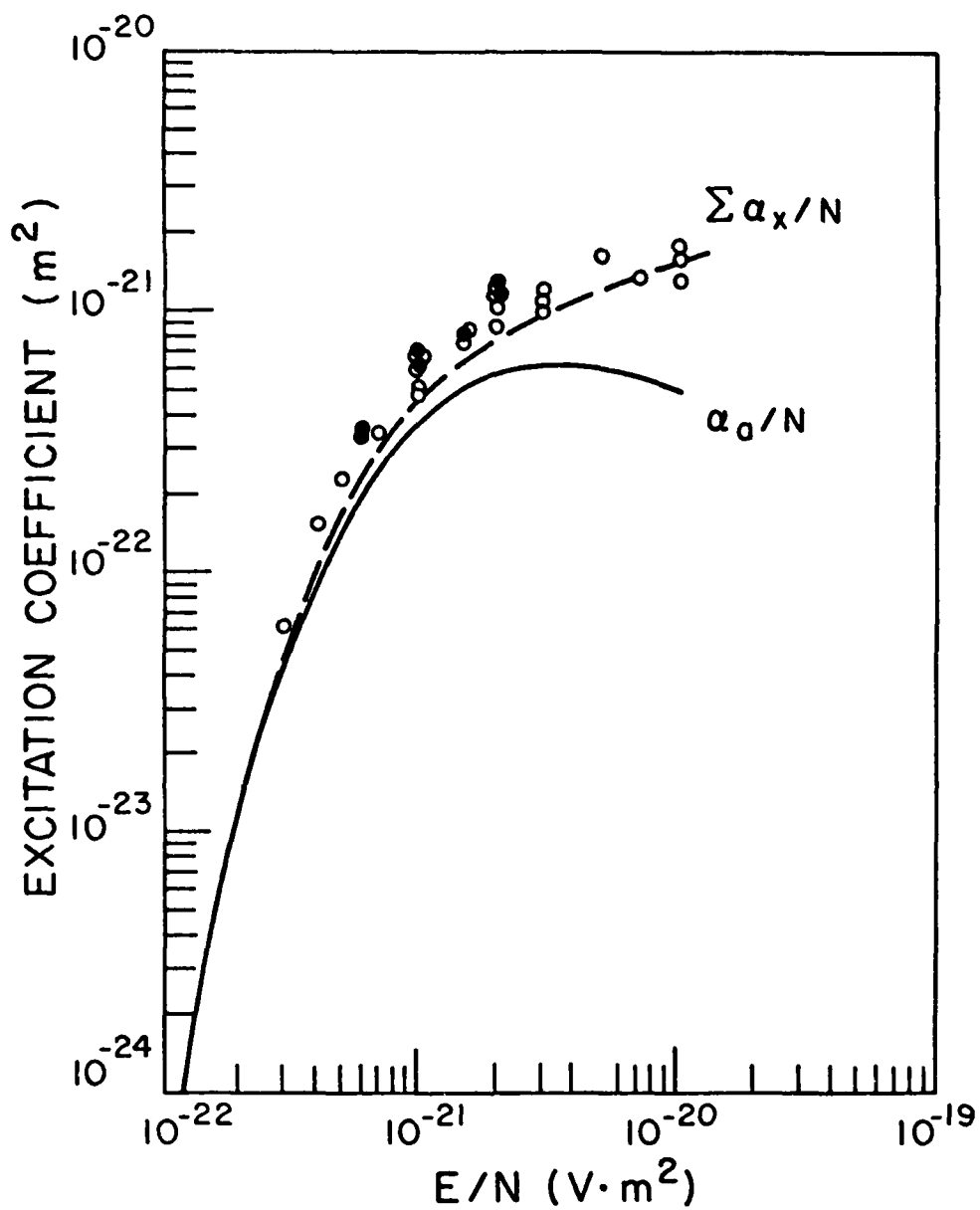


Figure 11. Experimental and Calculated α/N Values for 1% O_2 -99% Ar .

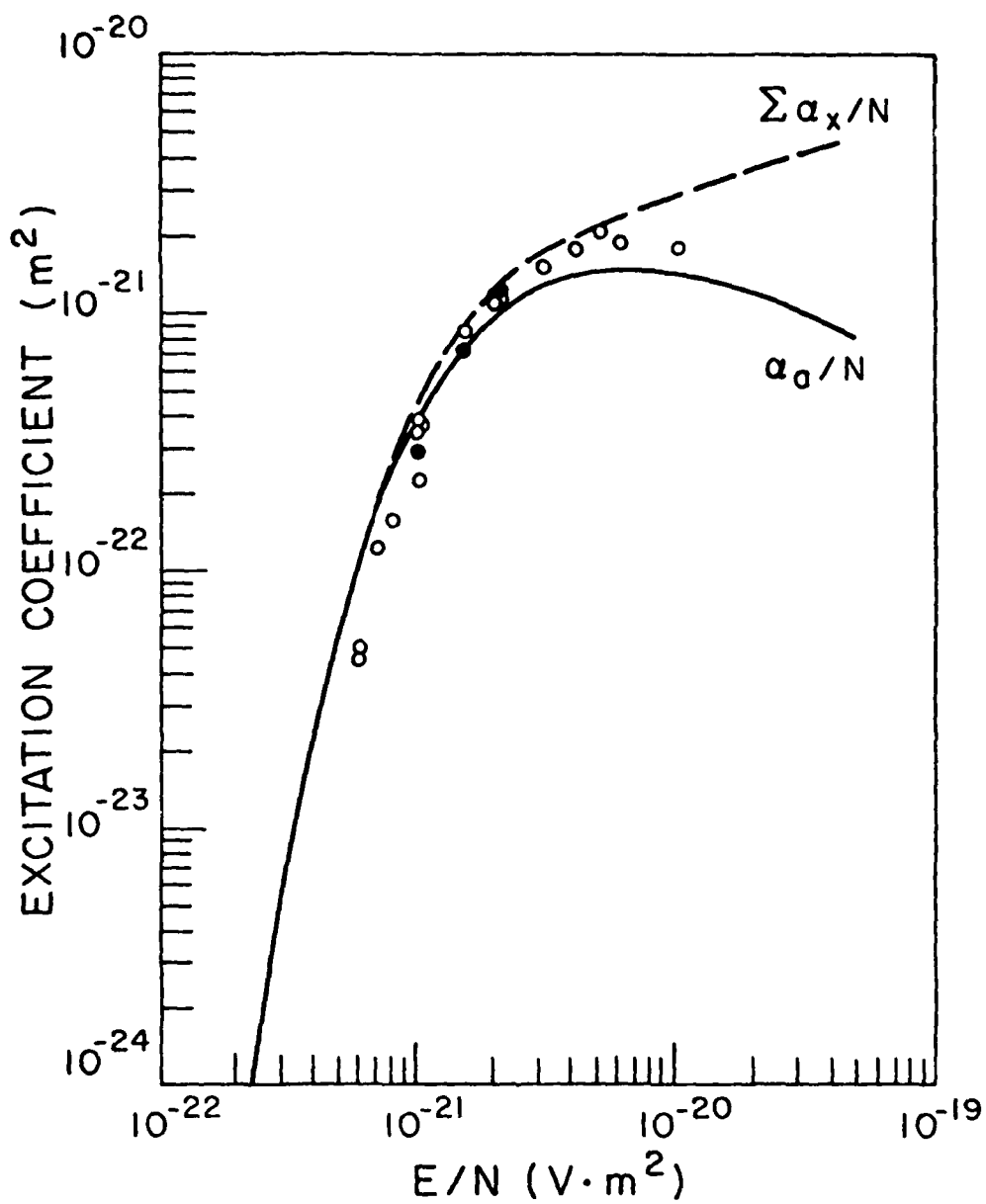


Figure 12. Experimental and Calculated α/N Values for 5% O_2 -95% Ar.

the transmittance of an IR-filter and the spectral intensity distribution of the black-body source has a maximum (5%). The total estimated uncertainty in α/N is 33% in this case instead of 25% in I.

The calculated values of α/N for direct excitation of the $O_2(a^1\Delta_g)$ state are shown in Figs. 11 and 12 by the solid lines. The dashed lines show the calculated results when collisional cascading from higher lying states is included. The efficiency of the cascading was assumed to be 100% as in I. From Figs. 11 and 12 it is seen that the measured rate coefficients are slightly higher than the calculated values for the O_2 concentrations of 1%, while the tendency reverses for 5% O_2 , especially for lower E/N values. The measured results agree with the calculated values when the cascading contributions at higher E/N values are included. The cascading in our E/N range, however, is mainly from the $b^1\Sigma_g^+$ state and its efficiency may be considered to be close to 100%.

SECTION V

CONCLUSIONS

The measurement of electron excitation rate coefficients described in this report provides a crucial set of data in the development of the ability to predict the behavior of electrons in pure oxygen or oxygen mixed with other gases. Devices and systems utilizing electron motion in oxygen include the proposed gas discharge excited oxygen-iodine lasers, electron beam propagation in the earth's atmosphere, ozone generators, and air insulation systems. In particular, these experiments provide for the first time quantitative measurements of the rates of production of the $O_2(a^1\Delta)$ metastable state under gas discharge-like conditions of mean electron energy and electron energy spread. Furthermore, these experiments show the usefulness of the drift tube technique for the measurement of excitation coefficients for metastable states which have very long radiative lifetimes and which radiate at infrared wavelengths where high sensitivity-low noise detectors are difficult to obtain and to operate.

The measured collisional deexcitation rate coefficient for $O_2(a^1\Delta)$ metastables by O_2 is in good agreement with published data. Our de-excitation rate coefficient for $O_2(a^1\Delta)$ by Ar is about twice the literature value. This could indicate the presence of higher than expected concentrations of impurities in our Ar supply. A test of this hypothesis will be made when we use a new Ar tank. We have no plans to attempt purification of the Ar, since our primary objective is the determination of excitation rate coefficients and since the data analysis includes the measurement of the rate of metastable destruction for each set of data.

The measured excitation coefficients for $O_2(a^1\Delta_g)$ excitation are within +30% of values calculated using our Boltzmann code and using our previously

recommended cross section sets for O_2 and for the buffer gas, Ar. Thus, our present predictive capability for rates of excitation of the $O_2(a^1\Delta)$ state is about $\pm 30\%$. We have no explanation for this systematic decrease in the ratio of measured to calculated excitation coefficients with increasing fractional oxygen concentration. Before undertaking a more extensive investigation of possible modifications of the electron collision cross section sets, we wish to extend the measurements of excitation coefficients to a wider range of fractional O_2 concentrations and to higher E/N. The higher E/N and higher mean energy data is of particular importance to an evaluation of the role of $O_2(a^1\Delta)$ excitation by cascading from higher excited states of O_2 . The higher mean electron energies are of practical importance because they are representative of discharge conditions of higher electrical power input.

In addition to the measurements of excitation coefficients at higher E/N and over a wider range of ratios of O_2 to Ar densities discussed previously, we recommend that:

(a) measurements of the rate coefficients for vibrational excitation of ground states of O_2 be made using, for example, the transfer of excitation from O_2 to CS_2 with subsequent emission at $6.5 \mu m$.

(b) a search be made for evidence of electron excitation of the metastable Herzberg states of O_2 , e.g., the $c^1\Sigma$ state which emits very weakly at wavelengths near 500 nm.

(c) measurements be made of the coefficients for dissociative excitation of O_2 using, for example, absorption of the OI resonance lines near 130 nm. We have recently received notice of support for this project from another agency.

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